p- to *n*-type conversion in GaSb by ion beam milling

G. N. Panin[a)]
Departamento de Fisica de Materiales, Facultad de Fisica, Universidad Complutense, 28040 Madrid, Spain

P. S. Dutta
Department of Physics, Indian Institute of Science, Bangalore-560012 India, and Instituto Nicolas Cabrera and Departamento de Fisica de Materiales, C-IV, Universidad Autonoma, 28049 Madrid, Spain

J. Piqueras
Departamento de Fisica de Materiales, Facultad de Fisica, Universidad Complutense, 28040 Madrid, Spain

E. Dieguez
Instituto Nicolas Cabrera and Departamento de Fisica de Materiales, C-IV, Universidad Autonoma, 28049 Madrid, Spain

(Received 21 August 1995; accepted for publication 16 October 1995)

Inversion in conductivity type of GaSb from *p*- to *n*- has been observed as a result of argon ion beam milling. Electron beam induced current (EBIC) measurements have been employed for detecting the type conversion. Enhancement in the luminescence intensity is seen after ion beam treatment. The type conversion is proposed to occur due to a combined effect of generation of native donors and gettering of native acceptors originally present in the as-grown samples. © *1995 American Institute of Physics.*

The III–V compound GaSb is gaining increasing importance for optoelectronic devices.[1] Promising device structures such as avalanche photodiodes (APD) with a high ratio of the ionization coefficients of holes and electrons have been demonstrated by earlier workers.[2] Until now, a majority of the *p*-*n* junction devices have been fabricated by epitaxial growth techniques.[3,4] From the device fabrication point of view, the ion milling (IM) technique is of utmost importance and has been widely used by numerous workers for other materials.[5–8] This is also important for mesa etching in devices.[9] Very limited attention has been devoted to the problem of ion implantation and related studies in GaSb.[10–13] Previous studies on ion implantation in GaSb have indicated swelling effects at the near-surface regions.[10] In the present investigation, we have carried out IM of *p*-GaSb by Ar^+ ions and studied its effect on the electronic properties by the spatial resolved EBIC and cathodoluminescence (CL) techniques. EBIC measurements with metal on *p*-GaSb structures could not have been performed due to Fermi level pinning close to the valence band edge.[1] This results in low barrier heights of metal on *p*-GaSb and therefore low efficiency of excess charge carriers separation. However, if as in other materials, IM causes local *p*- to *n*-type conversion, EBIC measurements should be possible. In such a case, an EBIC signal can be used to detect the existence of *n*-type layers and also as a characterization technique of the electrically active defects. To the best of our knowledge, such studies have not been performed on GaSb until now and have been the motivation of the present work.

Vertical Bridgman-grown single crystals of undoped *p*-GaSb (111) were used for our studies.[14] Prior to IM, the samples were mechanically polished to mirror finish with alumina powder of 0.02 μm. The samples were bombarded at an angle of 45° to the surface for 30 min at room temperature with 4 kV and 70 μm/cm^2 (ion beam current density) Ar^+ ions in an ion beam milling unit. The samples were rotated during the IM process. The ion irradiated samples were observed in a Hitachi S-2500 scanning electron microscope in the secondary electron (SE), EBIC, and CL modes. The EBIC measurements were carried out at liquid nitrogen temperature with 25 kV accelerating voltage and a beam current of 10^{-9} A. Electrical contacts for the EBIC measurements were provided by silver paste with gold wires to the treated region and back side of the sample. CL measurements were carried out at temperatures between 78 and 300 K by using a liquid nitrogen cooled North-Coast EO-817 Ge detector. The details of the experimental setup are presented elsewhere.[15]

Figure 1(a) shows a typical EBIC image of the IM sample. As stated above, the observation of EBIC contrast implies a type conversion caused by the IM treatment. The polarity of the EBIC signal corresponded to the formation of an *n*-type surface layer. Sub-boundaries usually present in as-grown samples can be seen in the figure. At higher magnification, uniformly distributed precipitates could be seen [see Fig. 1(b)]. The untreated samples did not show any EBIC image.

To supplement the EBIC studies and understand the nature of defects created during the IM treatment, CL measurements were carried out. IM causes an enhancement of the panchromatic CL emission in the irradiated area and its surroundings as shown in Fig. 2(a). CL intensity is higher at the center of the treated region and decreases radially. Apart from the increased luminescence intensity in the irradiated regions, uniformly distributed precipitates could also be seen under higher magnification as depicted in Fig. 2(b). It is

[a)]Permanent address: Institute of Microelectronics Technology and High Purity Materials, Russian Academy of Sciences, Chernogolovka, Moscow District 142432, Russia.

 0003-6951/95/67(24)/3584/3/$6.00

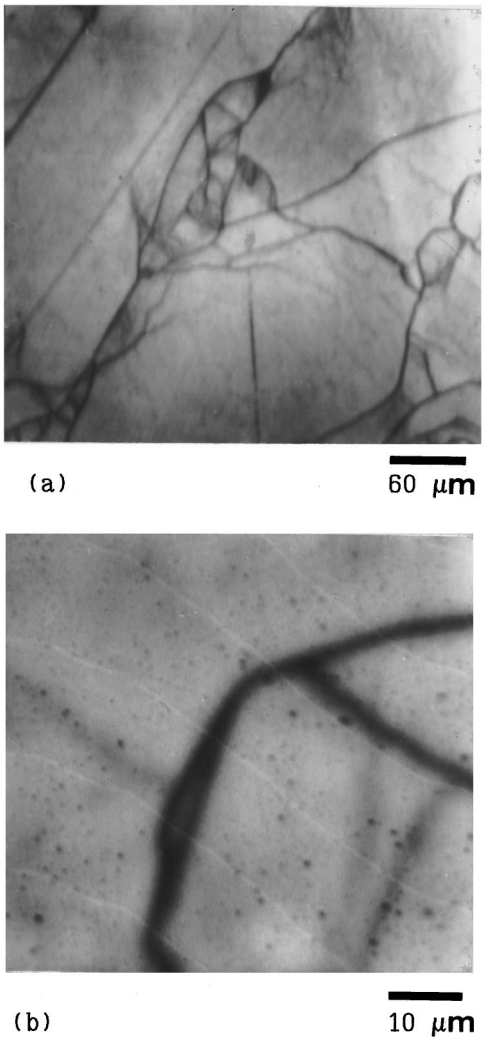

FIG. 1. EBIC image of p-GaSb after ion milling treatment with (a) 250× and (b) 1500×.

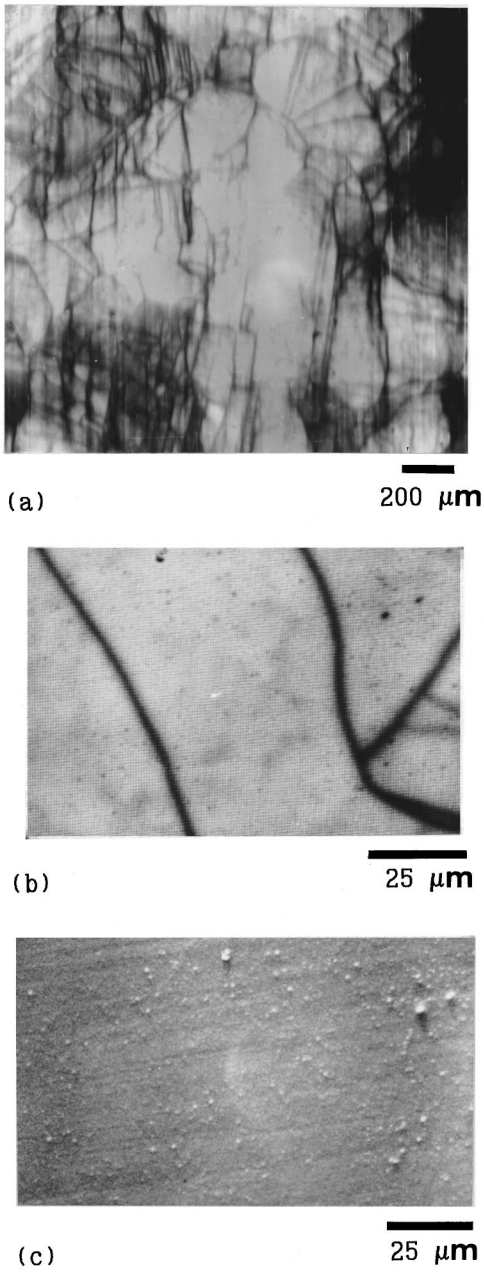

FIG. 2. CL images at the center of IM region with (a) 50× and (b) 600×, and (c) SE image of the IM region (600×).

worth pointing out that the CL image observed in Fig. 2(b) is similar to that of the EBIC image [Fig. 1(b)]. At exactly the location of a dark precipitate like the contrast in CL, the secondary electron image exhibits precipitates like topographic features as shown in Fig. 2(c). These extended defects were absent on the surface of the as-grown samples and are created during the IM treatment.

The CL spectra of the untreated and treated samples are shown in Fig. 3. Two broadbands at 777 and 757 meV could be seen in both the samples. Apart from the increased luminescence, no differences in the relative peak intensities or spectral features could be observed. The 777 and 757 meV transitions are associated with the native acceptors V_{Ga} and Ga_{Sb}.[16] From the CL spectra, the nature of the donor defect center could be implied. The increase in CL intensity after IM can be explained either by a bombardment induced increase in acceptor concentration or by the reduction of nonradiative recombination centers like grain boundaries and dislocations. The first possibility is ruled out as it would not result in an n-type surface region which is experimentally observed by EBIC. The latter process seems to be appropriate and can take place by gettering or decoration of nonradiative centers by any of the sputtered component from the bulk of the crystal. The appearance of precipitates could not be accounted for from any associated transition in CL spectra. These precipitates like extended defects resemble antimony precipitates usually seen in the CL images after annealing GaSb wafers in Sb atmosphere.[16] They, however require a more detailed structural examination for reliable identification.

Type conversion during ion milling has been mainly observed in II–VI compounds.[7,8] and attributed to reduction of native acceptors, which in turn increases the compensation by the unintentional donors. Ultimately, the net electrically active impurities become donorlike and a conversion to n-type ensues. The other possibility could be the generation

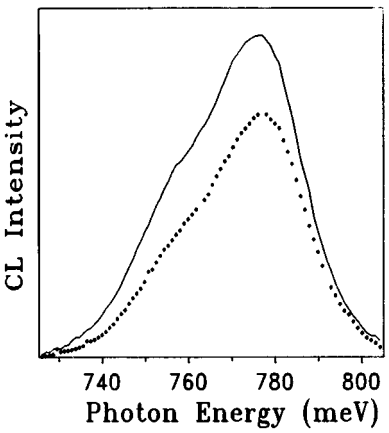

FIG. 3. CL spectra of untreated (dotted curve) and IM treated (continuous curve) *p*-GaSb.

of donor defects by ion bombardment. Previous studies on hydrogen plasma treatment of *n*-GaSb by Dutta *et al.*[17] have shown the creation of a thin surface defective layer with net donor concentration one order of magnitude higher than the background doping level. Such a defective layer introduces multiple donor states in the band gap.[17] The present EBIC and CL results can be explained by a similar effect in which IM introduces donor defects. The donor states thus introduced may be deeper from the band edge and do not appear in the CL spectrum due to the cutoff wavelength limitation of the experimental setup used. These donor defects can be of native origin and may be due to vacant antimony sites sputtered by the Ar^+ or related complex. The released antimony can also form precipitates as seen in the EBIC and CL images. Additionally during IM, the sputtered antimony can also occupy the Ga vacancies present in the as-grown crystal to form the antisite defect Sb_{Ga}, which is a donor center. This, in turn, will reduce the native acceptors (V_{Ga}). These transformations along with the unintentional donor impurities like Si will increase the compensation of the as-grown native acceptors and finally lead to the type conversion.

In conclusion, we have carried out IM of *p*-GaSb. The overall luminescence efficiency increases as a result of IM. As evident from EBIC measurements, IM results in type conversion from *p* to *n* of the near-surface region. The donor defects responsible for the type conversion are proposed to be of native origin. Our experiments do not yet permit us to conclude about the underlying mechanism which actually leads to the formation of the donor centers. Further studies will have to be carried out to well understand the phenomenon of type conversion. Nevertheless, for technological applications, the IM technique seems to be promising for the fabrication of reliable *p*-*n* junctions for APD and other optoelectronic devices.

G. Panin thanks Ministerio de Educacion y Ciencia for a research grant and P. S. Dutta thanks CSIR (India) for the award of Senior Research Fellowship. This work was partially supported by the Instituto Nicolas Cabrera, UAM, Madrid, Spain, through a Visiting Scientist Fellowship and by the DGICYT (Project PB93-1256), CICYT (IN93-0012) and ESP95-0148.

[1] A. G. Milnes and A. Y. Polyakov, Solid State Electron. **36**, 808 (1993).
[2] O. Hildebrand, W. Kuebart, and M. H. Pilkuhn, Appl. Phys. Lett. **37**, 801 (1980).
[3] F. Capasso, M. B. Panish, S. Sumski, and P. W. Foy, Appl. Phys. Lett. **36**, 165 (1980).
[4] A. Y. Polyakov, M. Stam, R. G. Wilson, Z. Q. Fang, P. Rai-Choudhury, R. J. Hillard, and A. G. Milnes, J. Appl. Phys. **72**, 1316 (1992).
[5] G. Bahir and E. Finkman, J. Vac. Sci. Technol. A **7**, 348 (1989).
[6] K. F. Chien, A. L. Fahrenbruch, and R. H. Bube, J. Appl. Phys. **64**, 2792 (1988).
[7] C. Blanchard, J. Favre, J. F. Barbot, J. C. Desoyer, M. Toulemonde, M. Konczykowski, D. Le Scoul, and J. L. Dessus, J. Appl. Phys. **68**, 3237 (1990).
[8] M. V. Blackman, D. E. Charlton, M. D. Jenner, D. R. Purdy, J. T. M. Wotherspoon, C. T. Elliott, and A. M. White, Electron. Lett. **23**, 978 (1987).
[9] T. Kohler, R. Martineau, T. Wong, and R. Rotoland, Proc. SPIE **244**, 153 (1980).
[10] R. Callec, P. N. Favennec, M. Salvi, H. L'Haridon, and M. Gauneau, Appl. Phys. Lett. **59**, 1872 (1991).
[11] S. J. Pearton, A. R. Von Neida, J. M. Brown, K. T. Short, L. J. Oster, and U. K Chakrabarti, J. Appl. Phys. **64**, 629 (1988).
[12] M. Perotin, L. Gouskov, H. Luquet, P. Abiale Abi, A. Sabir, and A. Perez, J. Appl. Phys. **68** 3756 (1990)
[13] Y. K. Su, K. J. Gan, J. S. Hwang, and S. L. Tyan, J. Appl. Phys. **68**, 5584 (1990).
[14] P. S. Dutta, K. S. Sangunni, H. L. Bhat, and V. Kumar, J. Cryst. Growth **141**, 44 (1994).
[15] B. Méndez and J. Piqueras, J. Appl. Phys. **69**, 2776 (1991).
[16] B. Méndez, P. S. Dutta, J. Piqueras, and E. Dieguez, Appl. Phys. Lett. **67**, 2648 (1995).
[17] P. S. Dutta, K. S. Sangunni, H. L. Bhat, and V. Kumar, Appl. Phys. Lett. **66**, 1986 (1995).